Organic polymers

5.1. Introduction

5.1.1 *Brief history*

Natural organic materials (wood, horn, skin, etc.) have been used since the dawn of humanity. Textile fabrication from vegetal fibers (linen, cotton, etc.) or from animals (silk, wool, etc.) reached an "industrial" stage from the Middle Ages onwards. The idea of changing raw matter by specific physical or chemical treatment (dyeing fibers, leather tanning, etc.) is practically as ancient as the applications themselves. In the 19th century, however, a new idea emerged: chemically modifying natural substances (fibers, skins, etc.) so as to make them into completely different from the natural forms. The two main processes are:

– *rubber vulcanization* (Goodyear 1839) which is open to a large variety of applications, such as air chambers (Dunlop 1888) and pneumatics (Michelin 1891);

– *cellulose nitration* (Parker 1862), which quickly led to the creation of celluloid (Hyatt 1869). At the time, it was believed that this was developed to replace the ivory used for making snooker balls.

Synthetic materials such as Bakelite (1909), which owe nothing to natural materials, would not appear before the 20th century. The great thermoplastics (polyethylene, poly (vinyl chloride), polyamides, etc.) came about between the 1930s and 40s. It was not until the 1950s and the boom of the consumer society that the real explosion in the polymer industry took place. This transition coincided with a new formation

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process: injection molding, which made it possible to make all sorts of objects at a quicker rate.

Is it possible to imagine consumer society without plastics, and the explosive development of plastics without injection? We will let historians answer these questions.

Scientific developments specific to polymeric materials have approximately a century of prehistory (1830-1930), a century in which researchers collected observations. For example, Joule, in 1857, reported on the specific character of the thermoelastic behavior of rubbers. However, it was not before the 1920s and 30s that the macromolecular structure in polymeric chains was firmly established (Straudinger, Nobel Prize). In the 1940s and 50s, P. Flory (Nobel Prize) built the physical foundations for polymer science by carrying out a harmonious fusion between structural chemistry, mechanical statistics and thermodynamics. At the beginning of the 1970s, P.G. de Gennes (Nobel Prize) introduced scaling laws, which gave a new impulsion to polymer physics.

Great synthesizing methods (ionic and radical polymerization, copolymerization, polycondensation) were already discovered before the end of WWII. In the 1950s and 60s, Ziegler and Natta (Nobel Prize) invented the stereospecific catalysis which quickly led to high density polyethylene and isotactic polypropylene, two of the most important industrial polymers in terms of tonnage. In recent decades, new synthesizing methods have emerged: group transfer polymerization, controlled radical polymerization, metallocene catalysis, etc. But the classic methods never stopped being perfected at the same time. This is what is meant when we speak of the 5^{th}, 6^{th} or even 7^{th} generation, in the case of polyethylenes for pipes or polypropylenes for injection molded parts. Each stage in this progression constitutes a significant level of progress in relation to the previous stage.

5.1.2. *Polymers among materials*

Where should we place industrial organic polymers in the category of materials? Here we are dealing with a sub-category with diffuse boundaries. It essentially contains organic substances, meaning those based on carbon chemistry, but we are also including semi-organic substances such a**s** organo-silicic polymers, or even inorganic substances such as polyphosphazenes. In this sub-category, only types with high molecular mass (typically higher than 10 kg mol^{-1}) carry the status of material (usable in solid state), hence the denomination of high polymer or macromolecule. However carbons (diamond, graphite) are excluded from this category. By their structure (non deformable networks) and their processing method,

carbons rather belong to the ceramic family. Finally, high polymers consist only of linear chain macromolecules (eventually branched) and deformable networks.

We can see that it is not easy to outline the precise contours of industrial organic polymers. However, three general characteristics allow us to distinguish them from other materials quite clearly.

5.1.2.1. *Organic characteristic*

This presents both great advantages and disadvantages. The advantage is the low density ($\rho \leq 2,5$) linked to the low atomic mass of constitutive atoms (C, H, O and N, essentially). We know that density plays an important role in dimensioning mechanical parts [ASH 01]. The disadvantage is that only a few organic structures can survive a short exposure to 400ºC, and a long exposure (10 years) to 250ºC. From this point of view, compared to ceramics and metals, polymers are "the bottom of the class". However, for an immense variety of applications, a ceiling temperature slightly above room temperature is sufficient. Thermal instability is not, then, an unacceptable defect.

5.1.2.2. *Polymers have a chain structure or an easily deformable mesh network*

Such a structure is characterized by the existence of strong covalent bonds in line with the chain (typical energy density: 2 to 10.10^{10} $J.m^{-3}$) and weak interchain (Van der Waals) bonds (typical energy density: 4 to 8.10^{8} $J.m^{-3}$). In every inorganic material, however, each atom is linked to neighboring atoms by strong bonds (covalent, ionic, or metallic) in the three directions of space. We see, then, that it is relatively easy to deform a polymer by modifying the chain conformation without breaking the strong bonds of the macromolecular skeleton. In contrast, in an inorganic material, every deformation must overcome the strong bonds. As a result, polymers are the least rigid materials (Young's modulus $E < 5$ GPa for the majority of isotropic polymers against $E \geq 10$ GPa for the majority of industrial inorganic materials). The "one-directional" character of the strong bonds in polymers is clearly demonstrated in the case of linear polyethylene: its Young's modulus is generally smaller than 1 GPa, and its ultimate stress is smaller than 40 MPa in the injection molded or quasi-isotropic extruded parts. Yet, as ultra-oriented fibers, (bullet-proof vests, for example) the modulus exceeds 100 GPa and the ultimate stress increases to higher than 1 GPa; properties which are similar to many metals. In the case of fibers, tensile loading directly strains the covalent bonds of the macromolecular skeleton, hence the observed properties.

Another important consequence of the low rigidity of polymers: their low thermal conductivity, which is primarily related to the propagation speed of the elastic waves in non-metallic materials. The polymers are, then, thermal insulators with generally a conductivity value in the order of 0.1 to 1 $W.m^{-2}.K^{-1,}$ whereas it is

approximately ten times higher in porous ceramics (concrete, brick, rock, glass, etc.) and one hundred to a thousand times higher in metals.

The characteristics of low rigidity and thermal insulation may constitute advantages or disadvantages, depending on the application considered. But, the advantage of polymers is that fillers can be incorporated into them (strengtheners or conductors) or they can be used as foams, so as to vary the considered properties in very wide proportions.

5.1.2.3. *Role of temperature and strain rate*

All materials are characterized by a major transition (glass transition for amorphous, melting for crystallines) which marks out the route of the solid state to the liquid state. Far from this transition, their mechanical properties are only lightly dependent on temperature (T) and strain rate ($\dot{\varepsilon}$.). On the other hand, the behavior is greatly influenced by these parameters around the transition. What clearly distinguishes polymers from other industrial materials is the fact that their glass transition (T_g) and melting (T_f) temperatures are relatively close to room temperature, typically -100°C $\leq T_g$ and $T_f \leq$ 400°C. We therefore expect the mechanical behavior to be more or less greatly affected by variations in temperature and loading rate (or loading times, in the case of static strains).

For all materials, let us summarize that:

$$0.5 \leq \frac{T_g}{T_f} \leq 0.8$$

In addition, we note that the melting enthalpy ΔH_f of polymers is not so different from that of metals. If we consider the equilibrium free energy of melting ΔG_f at constant pressure:

$$\Delta G_f = \Delta H_f - T_f \,.\, \Delta S_f = 0$$

$$\text{hence: } T_f = \frac{\Delta H_f}{\Delta S_f}$$

If the melting point of polymers is lower compared to inorganic materials, it is because the entropic term ΔS_f of the thermodynamic balance of melting is higher for polymers than for other materials. The relative importance of the entropic term

(linked to the diversity of conformations that can be adopted by a chain) is one of the most characteristic traits of polymer physics.

5.2. Polymer structures

Let us remember that by a polymer, we denote a substance which is made of macromolecules, whose structure is characterized by the repetition of a large number of a group of atoms, called structural unit, repetition unit, monomer unit or constitutive repeat unit.

5.2.1. *Three structure scales*

Generally, we distinguish three main structure levels, all three capable of having a major influence on the usage properties of the material. Each level concerns specific conceptual and experimental tools. The study of the properties of polymers is therefore nearly always a multi-scale problem, and the analysis of the structure is a multidisciplinary problem. The characteristics of these three structure levels are summarized in Table 5.1.

Structure level	**Entity**	**Main characteristics**	**Experimental tools**	**Conceptual tools**
Molecular	Monomer unit	Chemical reactivity Polarity/ cohesion Flexibility - dynamics	IR NMR	Organic chemistry
Macromolecular	Chain Network	Chain size Crosslink density	SEC Viscosimetry, – sol-gel	Physico-chemistry of polymers
Supramolecular	Crystalline lamella Spherulite Various heterogeneities	Size Rigidity Anisotropy	Microscopy Thermal analysis Radiation scattering	Material science

Table 5.1. *Three large structure levels (IR: infra-red spectrophotometry; NMR: nuclear magnetic resonance; SEC: steric exclusion chromatography*
Only the main analytical tools are quoted)

If polyamides have a higher melting point than polyethylenes, it is above all because the monomer unit of polyamides is much more cohesive than that of polyethylenes. The differences in polymer melting points are primarily linked to differences in structure on a molecular level. The other structure levels (molecular mass, lamella size, etc.) can indeed play a role, but to a second order.

If polyethylenes are much stronger than paraffins with the same molecular structure, it is because they have a higher molar mass. Here, the difference is found on a macromolecular level. The strength in solid state and the viscosity in molten state are both properties which are greatly influenced by the size of macromolecules.

If branched polyethylenes have a Young's modulus of 200-300 MPa, whereas linear polyethylenes have a modulus of 800-1000 MPa, it is because the linear polyethylenes are clearly more crystalline than the branched polyethylenes. Here, rigidity is essentially linked to crystallinity, meaning, to an ordered arrangement of chains, one in relation to another, on the supramolecular structure level.

5.2.2. *Molecular structure*

Organic synthesis can generate a quasi-inifinity of macromolecular structures. However, we can observe that the large majority of industrial polymers have been made from a relatively limited number of groups which seem to be the structure's building blocks. These groups can be classified according to their main function in the monomer unit. We distinguish the following functions:

5.2.2.1. *Ball joints*

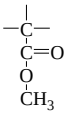
These groups allow for easy rotation, they allow the chain to be flexible

$-CH_2-$; $-CF_2-$; $-O-$; $-S-$

Substituted aliphatic carbons are equally ball joints, but their flexibility tends to decrease with the size and mass of lateral groups.

For example:

Polystyrene

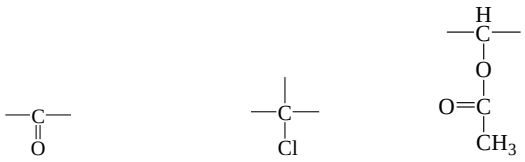


Polyacrylates

5.2.2.2. *Dipoles*

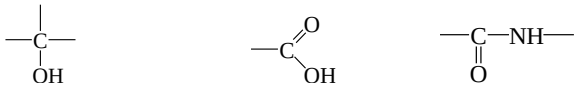
These groups display electric dissymmetry, therefore they will be able to more or less strongly contribute to cohesion (interchain interaction). We distinguish:

– moderately cohesive groups:



etc.

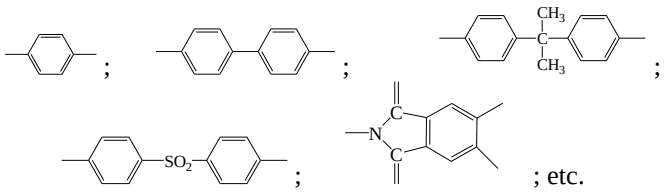
–strongly cohesive groups (hydrogen donors in hydrogen bonds):



etc.

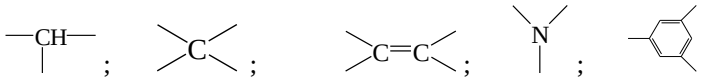
5.2.2.3. *Rigid elements*

These non-deformable groups will reduce the flexibility of the chains so much that they are bigger:



5.2.2.4. *Three-dimensional junctions*

The functionality group strictly higher than 2, is the basis for branching or crosslinking:



The two large physical properties which essentially depend on the molecular structure scale are *cohesion* and *chain flexibility*.

Cohesion is related to interactions (secondary bonds) between the chains. We characterize this by the cohesive energy density d_c defined by:

$$d_c = \frac{E_{coh}}{V}$$

where E_{coh} is the sum of all the intermolecular interaction energies in volume V of the material. d_e is an energy density, which can be expressed in pressure units.

For the majority of industrial polymers:

$250\ MPa < d_e < 800\ MPa$

At the low end of the interval, we find apolar polymers, such as polytetrafluoroethylene (PTFE), polyethylene (PE), polypropylene (PP) etc. At the top end of the scale, we find the most polar polymers, such as poly vinyl alcohol (PVAL), poly acrylic acid (PAA), etc.

We note that PTFE, PE and PP appear amongst the most hydrophobic polymers, while PVAL and PAA are soluble in water. Interactions between polymers and solvents are, in effect, controlled by the following rule (Hildebrand 1949): the closer the cohesive energy densities, the more the polymer interacts with the solvent.

We can define the solubility parameter by: $\delta = d_e^{1/2}$.

The solubility parameters of industrial polymers schematically vary between 13 $MPa^{1/2}$ (PTFE) and 27 $MPa^{1/2}$ (PVAL).

NOTE − The Hildebrand rule (maximum interaction for $\delta_{polymer} = \delta_{solvent}$) is only approximate. It is only used to indicate general tendencies.

Dynamic flexibility is defined as the chain's aptitude to deform under thermal agitation. The strain results from elementary rotations of the groups around the macromolecular skeleton bonds.

The glass transition temperature (T_g) which marks out the passage from low amplitude localized mobility to high amplitude cooperative mobility (see further down), is a good criterion for chain dynamic flexibility. Three main factors affect chain flexibility by hindering rotations:

– interchain interaction (meaning cohesion). We have seen that cohesion was considerably stronger in PVAL (T_g = 120°C) than in PP (T_g = 0°C) – two polymers whose monomer units have the same geometry;

– the size of lateral groups. This is why polystyrene (PS) has a T_g (105°C) higher than that for polyvinyl chloride (PVC, T_g = 80 °C), whilst the latter is more cohesive;

– the mass of non-deformable groups which increases the inertia of corresponding segments and makes their rotation more difficult. This factor tends to prevail in the high temperature domain where the interchain interactions tend to be negligible. We can observe this effect in the sequence in Table 5.2. The effect of the groups' mass is represented by the rigidity parameter F, defined by:

F = molar mass/number of bonds capable of rotation

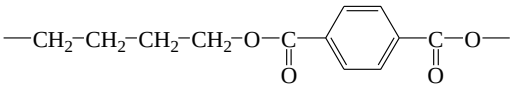
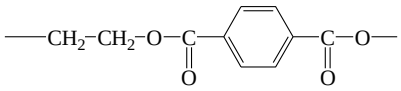
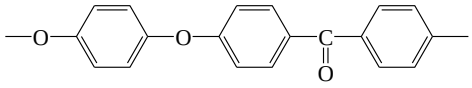
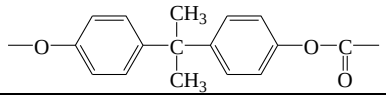
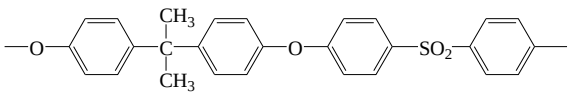
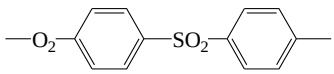
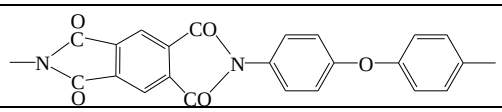
Acronym	**Structure**	**T_g (°C)**	**F ($g.mol^{-1}$)**
PBT		60	24.4
PET		80	27.4
PEEK		140	48
PC		150	63.5
PSU		190	110.5
PESU		210	116
PPMI		350	191

Table 5.2. *Characteristics of some polymers containing aromatic rings in the chain*

In Table 5.2, we consider that the isopropylidene (-C(CH_3)$_2$-) and sulfone (-SO_2-) groups are not ball joints because they block rotations aromatic nuclei on each side.

We see on Figure 5.1 that T_g tends to increase in a quasi-linear way with F.

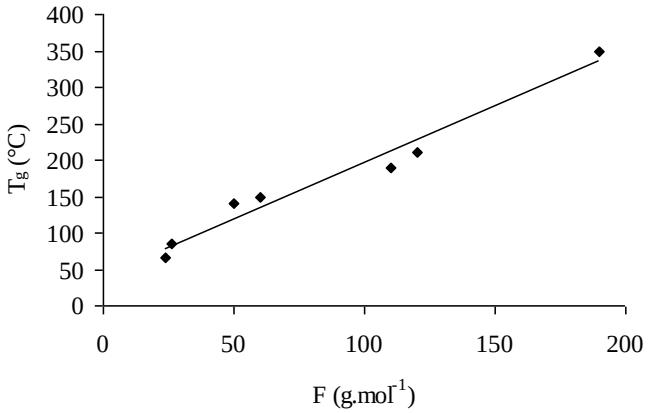


Figure 5.1. *Variation of vitreous transition temperature (T_g) with the rigidity parameter (F) (see text)*

Besides the physical properties above, *the molecular structure determines important aspects of the chemical properties*, particularly the reactivity to oxidation and hydrolysis. In the case of oxidation (thermally or photochemically initiated), the weakest structures are aliphatic CH bonds. In the case of hydrolysis, the reactivity is linked to the presence of hydrolysable groups, for instance esters, in the chains. We will return to these aspects in the chapter on aging.

5.2.3. *Order in the chain – Copolymers, stereoisomers, conformations*

5.2.3.1. *Copolymerization*

A polymer based on a single type of monomer (-(A)-$_n$) is called a homopolymer. The combination of two monomers A and B may result in a large variety of structures. The following can be distinguished:

– statistical copolymers :- A-A-B-A-B-B-B-A-A-A-B-A-A-B-B;

– alternate copolymers : - A-B-A-B-A-B-;

– block copolymers: - A-A-A-A-A-B-B-B-B-;

– grafted copolymers: –A–A–A–A'–A–A–A–A–A–
                                    |
                                    B–B–B–B–B–B–B–B–B–

Combinations of three (or more) monomers also exist, for example: ABS = acrylonitrile - butadiene – styrene. Very schematically:

– Alternate copolymers are equivalent to a homopolymer $[-(AB)-]_n$;

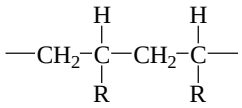
– Statistical copolymerization creates a material with intermediate physical properties between those belonging to the homopolymer $[-(A)-]_n$ and $[-(B)-]_n$. Therefore, one can use this to more or less tightly control the properties. One can also use statistical copolymerization to create a certain disorder in the chain, and thus limit crystallization;

– Block copolymerization may produce new properties: the sequences $[-(A)-]_n$ and $[-(B)-]_n$ are generally non-miscible. There is, then, a phase separation, but both phases are linked together by covalent bonds, which will ensure a good interfacial adhesion. This type of morphology is used in abundance to improve polymer impact strength (ABS, copolymers, ethylene-propylene, etc.);

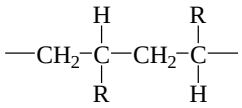
– Grafted copolymerization is particularly used to modify surface properties: printing, wetting, adhesion etc… when the polymer "trunk" is apolar, for instance polyethylene and the grafted polymer is highly polar, for instance polyacrylic acid.

5.2.3.2. *Stereoisomery*

When the monomer is dissymmetric (for example, vinyl monomer CH_2=CHR) it can give way to two types of sequence which are optical isomers:

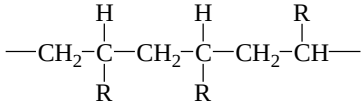


(isotactic diad)



(syndiotactic diad)

A given polymer can be regarded as a "copolymer" of isotactic and syndiotactic diads, and the triad at the junction of these two is "heterotactic":



When stereoregular sequences (iso, or syndicotactic) are short (lots of heterotactic junctions), the polymer is known as *atactic.*

Atactic polymers (for example polystyrene "crystal", poly (methyl methacrylate)) are completely amorphous.

Highly stereoregular polymers, predominantly iso or syndicotactic, can crystallize and reach high crystallinity ratios, eventually above 50%. Polymers with low iso or syndictactic predominance may lead to microcrystal formation in weak concentration, for example, 55% syndicotactic PVC having a crystallinity ration of 2 to 5 %.

5.2.3.3. *Conformations*

In liquid state, the chain is animated by ample movements which come from elementary rotations of the groups around the skeleton's aliphatic bonds. This can be seen, for example, in the case of a vinyl polymer (Figure 5.2).

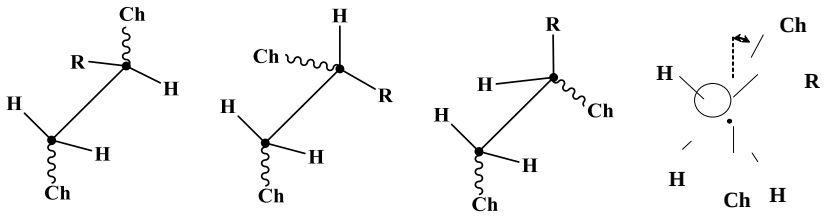


Figure 5.2. *Shifted representation of the trans conformation and two gauche conformations of a vinyl polymer. (Right): Newman representation. Ch = chain, R = lateral group. The carbon in front is used as a reference. We are actually studying the carbon at the back.*

The potential energy varies with the rotation angle θ according to a curve with the shape of Figure 5.3.

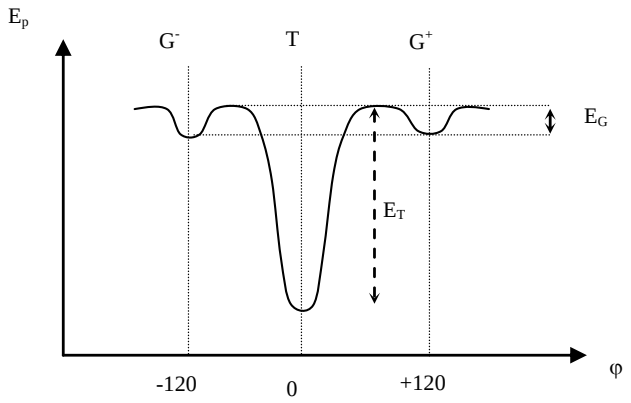


Figure 5.3. *Variation shape of potential energy with the rotation angle. NOTE: the potential well of gauche conformations in some cases can be deeper than for the one of trans conformation.*

Conformations can be experimentally observed by NMR.

Two quantities play a crucial role in a large number of physical properties:

– The height of the deepest potential well (E_T in Figure 5.3). This height determines the system's capacity to produce rotations around the considered bond. This capacity is expressed by the term:

$$R_D = \exp - \frac{E_T}{RT}$$

The deeper the potential well, (meaning a large E_T), the higher the rotation starting temperature. R_D can be called dynamic rigidity;

– The difference in height of trans and gauche potential wells :

$$R_S = \exp \frac{-(E_T - E_G)}{RT}$$

If this difference is high, the most stable conformation will prevail. If this difference is low, the trans and gauche populations will be close. We can see that the trans conformation leads to a plane zig-zag. We have diagrammatized the case by Figure 5.4.

Figure 5.4. *Diagram of three chain conformations: (a) all trans: the chain is a rigid rod; (b) widely predominant trans: the chain is weakly tortuous; (c) weakly predominant trans: the chain is very tortuous*

What we call the *persistence length* is the length of the trans-trans sequence. If the chain length is big in relation to the persistence length, it appears as a "random coil", which has an important characteristic: the end to end distance r. For a chain containing N segments of length l, one can define the chain characteristic ratio C_∞ , for a large N:

$$r^2 = C_\infty N l^2$$

In the majority of industrial polymers, C_∞ varies between 2 and 10. C_∞ is linked to R_S, which we can call the chain's static rigidity. If R_S is high, meaning that the chain is rigid, C_∞ is also high (polystyrene, poly(methyl methacrylate etc). If the trans and gauche conformations have close potential energies, C_∞ is low (polycarbonate, polysulfones). As we will see, static rigidity plays an important role in rheological properties and fracture behavior.

5.2.4. *Macromolecular architectures. Thermoplastics and thermosets*

We know a large variety of macromolecular architectures. The main ones are represented in Figure 5.5.

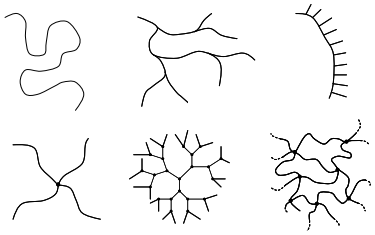


Figure 5.5. *Different types of macromolecular architecture: (a) linear chain, (b) chain with long branches, (c) chain with short comb-like branches, (d) star, (e) dendrimer, (f) network*

It is important to distinguish the species (a), (b), (c), (d) and (e), of finite size (molar mass generally between 10 et 10^4 kg.mol^{-1}) from species (f), of quasi-infinite size, since its boundaries are those of the considered object. For example, the epoxy matrix of an aeronautical part (20 kg matrix) is made of a single macromolecule

with a molar mass of: $M = 20 \times 6.02 \times 10^{23} = 12 \times 10^{24}$ kg.mol^{-1}. Here, the mole would be a quantity which is more relevant to astrophysics than physicochemistry.

For the processing expert, the boundary between material families is not topological, but simply linked to the size of the macromolecules. Schematically, for any polymer, there is a maximum size, which often corresponds to a molar mass M_L between 100 and 1,000 kg.mol^{-1}, such as:

– if $M < M_L$, a liquid state may be reached by raising the temperature, and the forming can be achieved by flow (injection, extrusion, calandering, rotomolding, welding, etc.). We, then, now have to deal with a *thermoplastic*;

– if $M > M_L$, then the liquid state cannot be reached, the material undergoes a thermal degradation before reaching this stage. In this case, flow forming can only be carried out on monomers, prepolymers or species which have not completely reacted, able to be taken to liquid state. Once forming is complete, the material can be "cured" in order to reach its definitive chemical form. Now, we are dealing with a *thermosetting polymer*. The synthesis-processing channels are therefore represented by Figure 5.6.

Thermoplastics:

Monomer(s) ➔ Polymerization ➔ Polymer ➔ Formed or processed ➔ Object finished or work achieved

Thermosetting polymers:

Monomer(s) ➔ Mixing ➔ Liquid object or workable mix ➔ Formed or processed ➔ Polymerization ➔Finished object or work achieved

Figure 5.6. *Representation of the elaboration ways in the case of thermoplastics and thermosetting polymers.*

5.2.4.1. *Monocomponents and bicomponents*

Applied to the construction domain, the previous double diagram demonstrates the differentiation between two modes of presenting the material [MOU 03];

– when it is enough to fluidify, soften through heating, or apply as an emulsion or solution, we use the product as proposed by the manufacturer directly, without chemical modification, and therefore we can speak of a *monocomponent* product;

– on the other hand, when it is necessary to mix two reactive components during use to achieve polymer synthesis, we are then talking about a *bicomponent.* This

term occasionally includes more complex mixes, for example when the product is loaded and the load is partly released, or when the reactional system contains a base, a catalyst and an accelerator which are to be mixed at the last moment and in the right order. Then, we can speak of a *tricomponent.*

That being said, we must not conclude from this that all monocomponents lead to thermoplastic materials, and bicomponents to thermosetting materials. Thus, the chemistry of polyurethanes allows a formulation of monocomponents which react with air humidity. These are actually bicomponents, to the extent where atmospheric water plays the secondary role of the monomer, or even "blocked isocyanate" based monocomponents which use the thermoreversability of the polyurethane formation reaction in order to release one of the polycondensation reactants. These two types of "monocomponents" may also lead to thermoplastics as well as thermosetting materials.

As can be seen, things are not as simple as we would like to think. At all costs, we must avoid turning the user into a "little chemist", meaning, letting him take the initiative in the preparation of the mix which is to be applied. This is why formulators have developed mixing guns, screw mixers, etc. which mean that we can obtain the desired product directly.

Additionally, there is no absolute identity between linear and thermoplastic polymers on one hand, and between tridimensional and thermosetting polymers on the other hand. Transparent semi-products made of cast PMMA, used in buildings, have molar masses higher than 1,000 $kg.mol^{-1}$ and cannot be formed by thermoplastic processing method. The monomer is cast in a mold, and polymerization takes place there within. This is then a matter of a thermosetting process. However, PMMA with a molar mass of ~ 50 $kg.mol^{-1}$ can be injection molded, for example, for the rear lights of a car. This is a thermoplastic. For some polymers such as polyamides or polyurethanes, both processing types can coexist for a same molar mass (thermoplastic and reaction injection molding RIM varieties). Here, the choice is made according the number of parts to be made, the RIM molds being noticeably lower in cost than the injection molds.

5.2.5. *Structure on a macromolecular scale*

5.2.5.1. *Linear and branched macromolecules*

For all types of architecture except networks, the size of the macromolecules is a fundamental characteristic. An industrial polymer is always a mix of different sized macromolecules, characterized by the molar mass distribution. $N_i = f(M_i)$. N_i is the number of i type macromolecules with a molar mass M_i.

There are experimental methods (SEC, MALTI-TOF *Matrix-assisted laser desorption/ionisation-time of flight*) which allow for a distribution of molar masses. From this, we can define averages, particularly the average in number:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

and the average in weight:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

It is easy to check that we still have $M_w \geq M_n$ and that the ratio $\frac{M_w}{M_n}$, known as the polydispersity index, is a measure of the broadness of the distribution.

In practice, the average molar masses are often determined by simpler and cheaper experimental methods than SEC or MALDI:

– For example, the chemical or spectrochemical titration of terminal groups; in principle:

$$[b] = 2\ M_n^{-1}$$

where [b] is the concentration of chains ends in the polymer;

– Viscometry:

$$\eta = k\ M_w^{\alpha}$$

where k does not depend on the molar mass and α is a scaling parameter which is not strongly dependent on the polymer's nature.

In the case of viscometry in solution, η is the intrinsic viscosity and $\alpha \sim 0.7$.

In the case of rheometry in molten state, η is the Newtonian viscosity and $\alpha = 3.4$.

In amorphous state, the chains are overlapped, entangled. The entanglements constitute nodes of a physical network which is responsible for the existence of a rubbery state above T_g and a ductile behavior in glassy state, below T_g (Figure 5.7.)

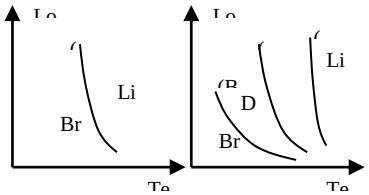
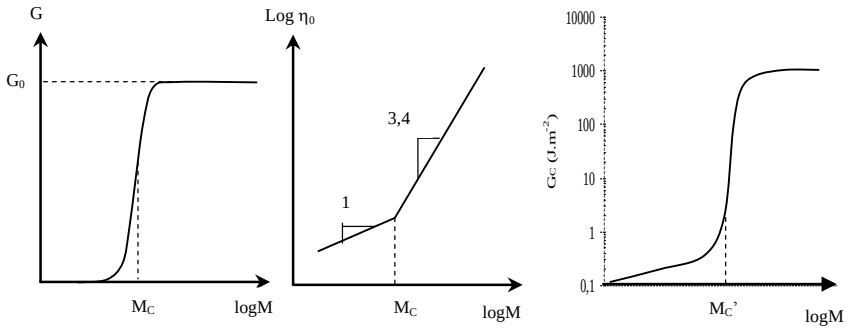


Figure 5.7. *Behavior domains in the time-temperature space. (G) is the glass transition (B) is the ductile-brittle transition (L) is the (pseudo) rubber-liquid transition. Left: unspecified amorphous material (polymer with low molecular mass included). Right: high polymer (typically $M > M_c$; M_c of the order of 10 to 100 $kg.mol^{-1}$).*

The entanglements only appear when the molar mass is higher than a certain critical value (Figure 5.8).



(a) (b) (c)

Figure 5.8. *Shape of the variation with molar mass: (a) rubber modulus, (b) Newtonian viscosity in molten state, (c) toughness in glassy state for a linear amorphous polymer. NOTE – $M_c' \sim 2$ to 5 M_c*

The shear modulus of rubber (G) tends towards an asymptotic value (G_0) when the molar mass tends towards infinity. G_0 is linked to the chain length between entanglements (molar mass M_e) by the Flory theory [FLO 53].

$$G_0 = \frac{RT\rho}{M_e}$$

where R is the gas constant and ρ the volumic mass.

M_e ranges approximately between 1.5 and 10 $kg.mol^{-1}$ for the majority of industrial polymers.

The relationship between M_e and structure on the molecular scale is now well known [FET 99]. M_e increases and chain tortuosity decreases when the chain transversal diameter increases.

5.2.5.2. *Networks*

A network is characterized by:

– the molar mass M_e of its elastically active chains (EAC), e.g. chains linked to network nodes at both ends;

– node functionality (the number of chains leading to a node).

An ideal network is one in which all the chains are elastically active.

We can then link concentration x in nodes with the EAC length:

$$x = \frac{2}{f.M_e}$$

There are only a few experimental methods which allow a determination of x or M_e.:

– the rubbery state elastic modulus in tension (E) or shearing (G) which lead to M_e thanks to the Flory theory mentioned above. However, in the case of elastomers, there are some corrections which must be made (see further). These corrections can be minimized or even canceled altogether when the modulus measurements are carried out on samples swelled by solvents;

– the equilibrium swelling ratio in a solvent which can be used to determine M_e, on the condition that the χ coefficient of polymer-solvent interaction is known [FLO 43] ;

– the glass transition temperature which is an increasing function of the crosslink density

For ideal networks, we can use Di Marzio's law [DIM 64]:

$$T_g = \frac{T_{gl}}{1 - K_{OM}.F.x}$$

where T_{gl} is the T_g of the copolymer (hypothetical) which contains all the structural elements of the network except the nodes ; K_{OM} is a universal constant (K_{OM} = 3 for trifunctional nodes). F is the rigidity parameter defined in section 5.1.2.

For incompletely cured networks, we can use the Di Benedetto equation [PAS 02]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda y}{1 - (1 - \lambda)y}$$

where:

− y is the conversion ratio (varying between 0 and 1);

− T_{g0}, T_g et$T_{g\infty}$ are T_g values pour y = 0, y = y and y = 1 respectively;

− and $\lambda = \Delta C_{p\infty} / \Delta C_{p0}$ where ΔC_p is the heat capacity jump at T_g, measurable by differential scanning calorimetry (DSC).

Contrary to what it usually claimed, networks are neither systematically more rigid nor more brittle than linear polymers. The only major difference lies in the fact that linear polymers can be brought to liquid state (if their molar mass is not too high), while the tridimensional polymers do not have a liquid state, whatever their crosslink density. Not all linear polymers are thermoplastics, but all tridimensional polymers are thermosets (although some can be hardened by irradiation, without raising the temperature).

5.2.5.3. *Crosslinking, gelation.*

We can schematically distinguish two types of cross-linking processes:

− a) those which come from a linear high polymer. Crosslinking, then, consists of "welding chains by points" at their ends if they have a particular reactivity, or on randomly distributed sites along the macromolecules (Figure 5.9);

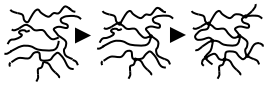


Figure 5.9. *Diagram representing linear macromolecular cross-linkage*

− b) those which come from small molecules where at least one of them has a functionality which is strictly higher than 2 (Figure 5.10).

Figure 5.10. *Diagram representing crosslinking process from small molecules*

In both cases, crosslinking represents the formation of macromolecules with a progressively high size and branching. The properties, particularly rheological properties, do not vary in a monotonic way with the chemical conversion (Figure 5.11).

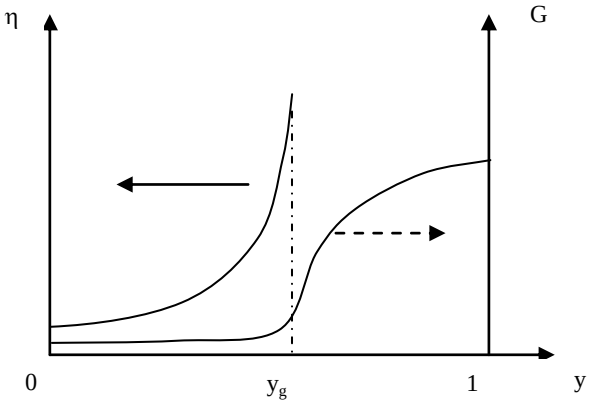


Figure 5.11. *(Left) Viscosity and (right) shear modulus of the reactional medium during crosslinking*

Gelation point ($y = y_g$) relates to the moment when a quasi-infinite macromolecule (i.e. size in the order of the reactor size) appears in the medium. It is a percolation threshold. In the case of processing by flow, the gelation point is the "point of no return". On this side, forming or processing is possible. Beyond this point, it is impossible.

The value of y_g depends on the size and functionality of the reactive molecules. In the case of crosslinking linear macromolecules of initial molar mass M_{W0} (figure 5.8), we have:

$$y_g = \frac{1}{M_{w0}}$$

We can see that the system gels at low conversion ratio.

In the case of a bicomponent (A+B) system where the reactant functionalities are respectively f_A and f_B and where A and B are in stoichiometric ratio, it can be written [FLO 53]:

$$y_g^2 = \frac{1}{(f_A - 1)(f_B - 1)}$$

For example, in the case of diepoxide crosslinking ($f_A = 2$) by a diamine ($f_B = 4$), then $y_g = 0.58$.

5.2.6. *Structure on a supramolecular scale*

5.2.6.1. *Amorphous phases and glass transition*

Let us consider an unspecified polymer. Brought to a sufficiently high temperature, it will be found in a liquid or rubber state, meaning in a state of maximum disorder where the chains, in configuration of random coils, are largely overlapped/entangled. When it is cooled, for example at a constant speed $\dot{T}$ of temperature decrease, it tends to crystallize in order to minimize its potential energy, as with all substances. However, this tendency can be contradicted, or even completely stopped. This leads us to distinguish the following four polymer families:

− *family A_1:* the chemical structure which is too irregular, is incapable of being in order, whatever the cooling conditions. All atactic polymers, many statistical copolymers, and nearly all the thermosetting polymers belong to this family;

− *family A_2*: with the cooling rate $\dot{T}$ being too high in relation to the crystallization rate, the material does not crystallize but, with a slower cooling process, crystallization then becomes possible. PET (poly(ethylene terephthalate) is part of the polymers which can be easily obtained in an amorphous or semi-crystalline state. Polycarbonate (PC) is always formed in an amorphous state, but if it is maintained at a temperature higher than its glass transition temperature for long time enough, it is susceptible to crystallization (which has no practical interest);

− *family C_1*: in the range of normal cooling rates, the polymer crystallizes. We can vary the crystallization rate by playing with $\dot{T}$. Polypropylene (PP) and

polyamides (PA) both belong to this family which differs from family A_2 only because it is difficult to acquire 100% amorphous samples;

− *family C_2*: the polymer will crystallize whatever the cooling rate (though this is limited anyway by the weak thermal conductivity of the material). Polymers with a symmetric monomer unit belong to this family.

$-CH_2-CH_2-$	$-CH_2-CF_2-$	$-CF_2-CF_2-$	$-CH_2-O-$
(PE)	(PVDF)	(PTFE)	(POM)

The symmetry of the monomer unit favors quick crystallization.

Let us now consider the A_1 type amorphous polymers, and return to the cooling experiment (at $\dot{T}$) from a liquid state. There are two main approaches for its behavior: one based on free volume considerations, and another based on chain configuration entropy considerations.

5.2.6.1.1. Free volume theory

According to this theory, the mobility (cooperative mobility, i.e. motions of relatively large amplitude) of the chain segments is only permitted because a fraction f of the volume is free. This fraction can be defined by using dilatometric data (Figure 5.12).

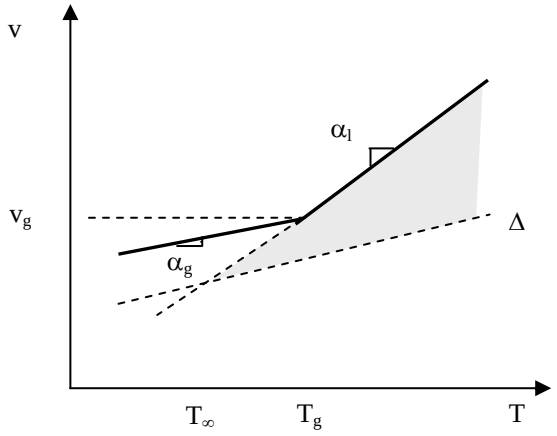


Figure 5.12. *Definition of the free volume fraction (shaded area)*

The dilatometric behavior of the material is represented, as a first approximation, by two half-straight lines coming from the point of glass transition. In glassy state,

the expansion coefficient α_g is generally between 1 and $4.10^{-4}.K^{-1}$. Expansion is essentially linked to atom vibrations around their equilibrium positions. There are no (or few) rotations.

The expansion coefficient in liquid/rubber state α_l is generally between 5 and $10.10^{-4}.K^{-1}$. As a first approach, we could say that the excess free volume allowing motions of cooperative rotations in liquid/rubber state is equal to the excess volume created by the expansion $f = \alpha.(T-T_g)$ at $T > T_g$ with $\alpha = \alpha_l - \alpha_g$. However, detailed studies show that a significant mobility stays at T_g, which leads to propose:

$$f = f_g + \alpha.(T-T_g) \qquad \text{(the order of quantity } \alpha \text{ is } \sim 5.10^{-4}\ K^{-1})$$

f_g has a quasi-universal value of 0.025 (in other words, the free volume constitutes 2.5% of the total volume at T_g).

The free volume is canceled at T_∞ as:

$$C_2 = T_g - T_\infty = \frac{f_g}{\alpha} \sim 50\ K$$

Vitrification (transition from liquid to glassy state) can be explained by the fact that during the cooling process, the material contracts until the fraction of free volume becomes lower than an (f_g) volume where cooperative motions become impossible. Thus, the chains become fixed, and only localized motions with low amplitude remain.

5.2.6.1.2. Entropy theory

Let us consider the population of a kind of conformation, gauche for example, whose molar fraction is [G]. An equilibrium value [G] corresponds to any temperature, depending on the static flexibility of the chain. During the cooling process from T to $T-\Delta T$, the conformation fraction moves from [G] to $[G]-\Delta[G]$. In other words, a section of the gauche conformation transforms into a trans conformation. However, the corresponding rotation is not instantaneous and its rate decreases when the temperature decreases.

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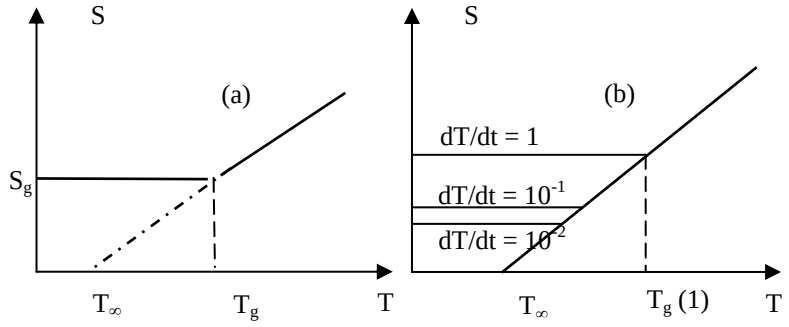


Figure 5.13. *(a) Shape of variations in entropic chains around T_g*
(b) Influence of the cooling speed

We can make the following observations:

– The glass phase is out of thermodynamic equilibrium (it is therefore likely to evolve slowly by moving towards this equilibrium, a process which is called "physical ageing" or "structural relaxation".

– Since vitrification is a dynamic phenomenon, the weaker $\dot{T}$, the longer it will take (at a lower T_g) for the vitrification to occur (Figure 5.13b);

– By extrapolating the equilibrium line (in liquid state) we are cutting the temperature axis at $T_\infty = T_g - C_2$ with $C_2 = 50$ K. In theory, T_∞ is the T_g that we would expect with an infinitely weak cooling speed. Actually, it is difficult to observe T_g variations more than 20 K in an experiment, taking into account the excessive duration of tests and the difficulties of controlling extremely low cooling rates.

5.2.6.1.3. Other physical approaches

The theory of quasi punctual defects [PER 01] is an interesting alternative to the aforementioned theories. At this current time, molecular modeling is rapidly developing and is starting to give us results for glass transition.

5.2.6.1.4. Glass transition temperature in practice

T_g depends on the time scale where it is determined, it hardly varies in the range of temperature variation rates which are accessible to the normal approaches of thermal analyzes (typically 10^{-2} to 100 K.min^{-1}). The data found in literature on the subject generally refers to measurements done between 1 and 20 K.min^{-1}. The three

most commonly used methods to determine T_g are shown diagrammatically in Figure 5.14.

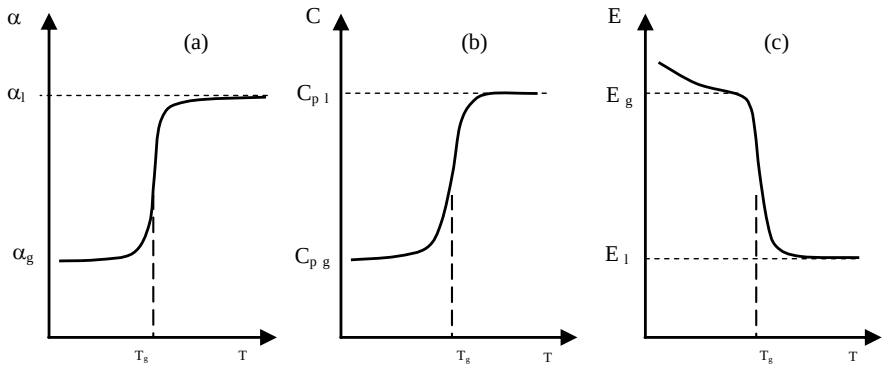


Figure 5.14. *Shape of volumic expansion ratio variations (a) of heat capacity (b) and of Young's modulus (c) around T_g. NOTE: In the case of the modulus (c), we observe that transition α associated with glass transition T_∞ increases when the measurement frequency (dynamic modulus) increases.*

The order of magnitude of boundary values found in Figure 5.3 is given in Table 5.3.

Characteristic	Glassy state	Rubbery state
α	(1 to 5).10^{-4} K^{-1}	(5 to 10).10^{-4} K^{-1}
C_p	(1,6 ± 0,1) $kJ.kg^{-1}.K^{-1}$ (a)	(1,9 ± 0,4) $kJ.kg^{-1}.K^{-1}$
E	~ 1 GPa	0.1 to 10 MPa

Table 5.3. *Physical characteristics on both sides of T_g*
NOTES– (a): for halogen polymers C_{pg} ~ (1.0 ± 0.1) $kJ.kg^{-1}.K^{-1}$
(b): for structure relationships –T_g see section 5.2.2 above

5.2.6.1.5. Morphology of amorphous polymers

Some types of amorphous polymers (“crystal” PS, “crystal” PVC, PMMA, poly(dimethylsiloxane)) are transparent and, in some cases (PMMA), are limpid even so at great thicknesses. These materials appear as “fixed” liquids.

Other amorphous polymers (vulcanized rubbers, thermosetting polymers, thermostable polymers, etc.) are opaque in strong thicknesses, and translucid in weak thicknesses. The fact that they diffuse light may be linked to fluctuations in the refractive index, revealing heterogeneities which are typically higher than 100nm. However, even in these materials, only very sophisticated methods of analysis allow for precise characterization of these heterogeneities which have been the subject of much controversy for a long time, in the case of epoxy networks, for example [PAS 02].

In the case of diphasic systems (polymer blends, copolymers, block copolymers), a clearly more contrasted morphology can be observed by electron microscopy or atomic force microscopy. One of the most beneficial morphologies, in terms of mechanical properties, is a morphology where nodules with low dimensions are dispersed in the matrix (Figure 5.15).

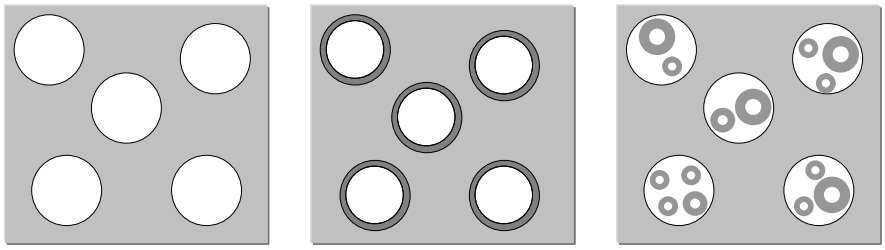


Figure 5.15. *Diagram showing three current types of nodular morphology. (a) Simples nodules (b) core-shell nodules (c) Inversion phase nodules. The nodule sizes in the 100 nm – 10 µm interval are relatively common.*

Other morphologies (in labyrinths, onions, etc.) can also be observed.

5.2.6.2. *Crystallization and melting processes*

Crystalline phases are characterized by the existence of a melting point T_f and a higher packing density than the corresponding amorphous phases, with the volumic mass ratios ρ_c/ρ_a ranging between 1.05 and 1.25. When a polymer can easily be acquired in amorphous or crystalline form (PET or PEEK, for example) it is possible to demonstrate through experiments the difference in behavior between the amorphous and crystalline phases (Figure 5.16).

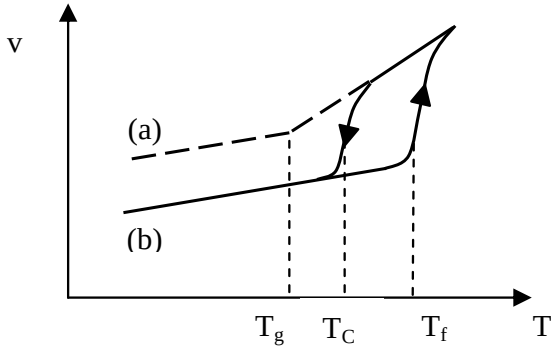


Figure 5.16. *Diagram showing volumetric behavior of a polymer in amorphous state (dashed lines), in 100% crystalline state (continuous lines). The arrow indicates the direction of the temperature variation*

The graph displays an important hysteresis: crystallization occurs at a temperature which is clearly lower than the melting temperature. The melting temperature is an instantaneous phenomena, whilst crystallization in a kinetic phenomenon.

Thermal behavior is similar to dilatometric behavior (Figure 5.17a). Regarding elastic properties, the crystalline phase modulus is slightly higher than that for glassy amorphous phases and around 1,000 times higher than for rubbery amorphous phases (Figure 5.17b).

The crystallinity ratio χ_c can be determined from density measurement:

$$\chi_c = \frac{\rho_c}{\rho} \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

It can be also determined by differential scanning calorimetry (DSC) (Figure 5.16a), by X ray scattering and, in some cases, by a spectrochemical method (IR, RMN).

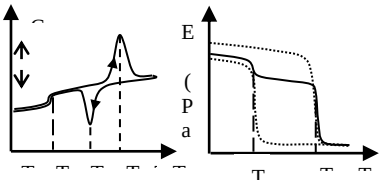
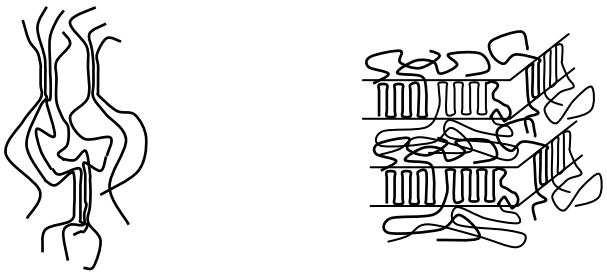


Figure 5.17. *Semicrystalline polymers: (a) Specific heat variation with temperature during a $T_0T_1T_0$ cycle. The melting peak is endothermic, the crystallization peak is exothermic. The melting peak surface can be used in certain cases to determine the crystallinity ratio. When the crystallinity ratio is high, the jump of C_p at T_g (linked to the amorphous fraction) can be quite undetectable (b) Modulus variation with temperature for a semicrystalline polymer (full line) for the same polymer which is 100% crystalline (Crist) and 100% amorphous (Am). The scale is only indicated to give the order of magnitude.*

Crystalline morphology can take various forms, with the elementary structure being either the fringed micelle or plate like lamellae (Figure 5.18).



(a) (b)

Figure 5.18. *Diagram of crystalline morphology. (Left) fringed micelles (samples generally in small crystalline amounts). (Right) lamella resulting from the crystallized chain folded on itself*

The long period l_p can be determined by small angle X ray scattering (SAXS). The lamellae thickness can be determined from the melting point (Thomson relation).

$$T_f = T_{f0}\left(1 - \frac{2\sigma}{\Delta H_f . l_c}\right)$$

where T_f is the melting temperature of a crystal with infinite thickness, σ is the surface energy and ΔH_f the melting heat. l_c generally varies between a few nanometers and a few tens of nanometers.

When the crystallinity ratio is raised, the lamellae form ribbons and are radially organized into spherulites growing from a nucleation center.

5.3. Additives and fillers

Organic polymers are rarely used pure, with the exception of a few organic glasses. Additives and fillers are incorporated into the polymers to adjust their properties so they can be adapted for specific usage. In principle, additives are dissolved in the polymer, whereas fillers are insoluble and thus form a diphasic system (composite) with the polymer.

5.3.1. *Additives*

5.3.1.1. *Processing aids*

The most commonly used additives are lubricants, such as fatty esters, amides or acid salts. They are used in weak concentrations, just like anti-static or anti-blocking agents which are particularly used in films.

5.3.1.2. *Stabilizers*

Some (thermal) stabilizers are essentially used so as to protect the polymer at higher temperatures, when it is being processed. Anti-oxidants (phenols, amines, sulfides, phosphites, etc.) are used in virtually all aliphatic polymers, with the exception of fluorides which are intrinsically stable. Certain polymers, particularly PVC, involve specific stabilizing methods based on the principle of substituting labile chlorine atoms (soaps containing Ca/Zn^{++}, organostannics, etc.)

Anti-UV stabilizers are used in external exposure applications. 2 hydroxy benzophenones, hydroxyphenyl benzotriazoles**,** substituted acrylonitriles, and

benzylidene malonates are the most frequently used UV absorbers, in concentrations higher than 1%.

5.3.1.3. *Plasticizers*

Plasticizers are generally used to soften organic glass (dioctyl phthalate type esters in PVC, aromatic chlorides in polycarbonate, etc.). 30% of dioctyl phthalate transforms the initially rigid PVC (T_g = 80°C) into an elastomer (T_g ~ -50°C) which can be used to create textile coatings, flexible tubes, soft toys, etc.

5.3.1.4. *Anti-flammable agents*

These agents are used to improve the fire resistance of polymers which are considered flammable in their natural state. These are a mixture of species, such as aryl phosphates, halogen molecules and inorganic fillers such as antimony trioxide, aluminum trihydrate, etc (see the chapter 8).

5.3.1.5. *Various additives*

Plastosoluble dyes, anti-static agents (quaternary ammoniums, for example), bleaching agents, etc., can be seen in certain particular applications.

5.3.2. *Fillers*

5.3.2.1. *Micrometric granular fillers*

Some fillers are used as white pigments, (TiO_2, Zn0), black pigments (carbon black), etc. Pigments are generally used in low concentrations.

Other fillers with weak aspect ratios (talc, calcium carbonates, etc.) are often used as “dilutants” in the polymer matrix due to their low cost. Generally, they have a tendency to increase the rigidity and softening temperatures under mechanical loads. But on the other hand, they are disadvantageous in terms of ductility and resilience.

Fillers with higher aspect ratios, such as mica plates or acicular fillers (wollastonite) sometimes greatly increase the modulus and resistance to fracture.

Some fillers play a particular role, such as making a polymer which was initially an insulator into a conductor of electricity (carbon black, metallic powder), making it opaque to X-rays (Ba sulfate), to neutrons (borates), etc.

5.3.2.2. *Nanometric fillers*

At the current time, research on nanometric sized fillers (montmorillonite, etc.) is developing quickly. In weak concentrations, these fillers can act as strengtheners (carbon nanotubes), greatly decrease gas permeability, etc.

5.3.2.3. *Fibrous fillers*

Glass, carbon or aramide fibers (Kevlar, for example), either long (impregnation process) or short (injection, extrusion, etc.) have a heightened strengthening effect which is linked to their particularly beneficial aspect ratio, and are widely used as much in thermosetting matrices as in thermoplastic matrices.

5.4. Processing properties

5.4.1. *Thermoplastics*

First of all, let us remember the shape of variations in the shear modulus G with temperature, G being determined in a fixed time scale, for example by dynamic measurements at a frequency of 1Hz (Figure 5.19).

Curves G=f(T) allow us to define two transitions:

– *glass transition* (T_g) drawing out the passage from a glassy state to a liquid or rubbery state, with a drop in the modulus by a factor of 100 or more. T_g depends on the molar mass according to the Fox-Flory equation:

$$T_g = T_{g\infty} - \frac{k_{FF}}{M_n}$$ with k_{FF} in the order of 10 to 100 K.mol.kg^{-1}

k_{FF} tends to increase with the dynamic rigidity of the chains, like $T_{g\infty}$;

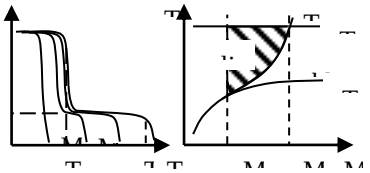


Figure 5.19. *(a) Modulus-temperature curves for different molar masses: $M_1 < M_c$ $M_2 > M_c$ $M_3 > M_2$ $M_4 > M_3$. (b) Phase diagram coming from figure (a)'s curve beam, where the thermal degradation temperature T_D has been added*

– « *liquid-liquid » transition* (T_L) draws out the path from a rubber to liquid state. This is a diffuse transition, without discontinuity of thermodynamic quantities. We can, then, consider this as an isoviscosity point. For $M < M_c$, T_L is equal to T_g. For $M > M_c$, $T_L - T_g$ (the rubber plateau length) rapidly increases with M.

The degradation temperature T_D must also be arbitrarily defined. Beyond this temperature, the polymer's thermal degradation (in the considered time scale) then becomes unacceptable with regard to the user.

The intersection between curves T_L and T_D relates to a molar mass M_D which has the following meaning: M_D is the highest molar mass which can be brought to a liquid state, which allows for material processing by flow. For $M > M_D$, this material degrades before reaching the liquid state. Let us not forget that for $M < M_c$ the material is extremely brittle and cannot be used for a mechanical application.

There are many polymers for which $M_D < M_c$, in other words, for which there is no usable molar mass interval (PVC, PP, etc.) Fortunately, additives such as thermal stabilizers (acting on T_D) allow boundaries of different physical states, as shown in Figure 5.19b to be displaced, and for "processability windows" to be opened, as represented by the curvilinear triangle cross-hatched on the figure.

Let us recall that liquid state viscosity depends on the molar mass according to the scaling law $\eta_0 = K.M^{3.4}$ where K depended on temperature and material chemical structure, and η_0 is the Newtonian viscosity. Curves $\eta = f(\dot{\gamma})$ have the shape of Figure 5.20.

In branched samples, the Newtonian plateau tends to decrease and even disappear. In the liquid state, injection, extrusion, rotomoulding and calendaring are performed, as seen in the cross-hatched window of Figure 5.19b. These methods differ by the imposed shear rate, and require adapted viscosity ranges. For example, injection, which is characterized by particularly high shearing rates, requires viscosities (molar masses) which are lower than extrusion. Plastic manufacturers commercialize grades which are adapted to such or such processing methods.

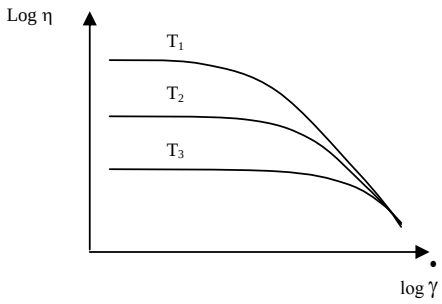


Figure 5.20. *Shapes of curves Log(viscosity) = f[log (shear rate) at different temperatures $T_1 < T_2 < T_3$. At a given temperature, the Newtonian plateau is as long as the molar mass is low.*

Thermoforming is the only processing method where the material is in a rubbery state and can be subjected to large strains without rupture.

5.4.2. *Thermosetting polymers*

As we have already seen, we can characterize the evolution of a material during its crosslinking process on the one hand by the conversion ratio y of the reaction, and by the glass transition temperature T_g on the other. By plotting T_g versus y, we obtain Figure 5.21.

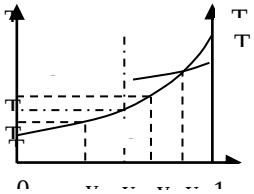


Figure 5.21. *Diagram Temperature – conversion ratio relative to thermosetting hardener*

The T_g of the starting mixture is T_{g0}. The T_g of a totally crosslinked material is $T_{g\infty}$. During the reaction, T_g increases according to a hyperbolic law (see above, section 5.2.5.3.) which is represented by the full line on the figure. The material is characterized by its gelation point at conversion ratio y_g.

Let us consider various cases of isothermal treatment:

– if $T \leq T_{g0}$, the reactive mixture is in glassy state. With the molecular mobility extremely reduced, the reaction does not occur. The reactive mixture can (and must) be preserved at $T < T_{g0}$;

– if $T_{g0} < T_i < T_{gg}$, and the reactive mixture is initially in liquid state, it will react; however, at the conversion ratio y_1, if T_g is equal to the imposed temperature, it will go to the glassy state (vitrification) and the reaction will stop;

– if $T_{gg} < T_2 < Tg_\infty$, the reactive mixture reacts, gels for $y = y_g$ but keeps enough mobility, in the rubbery state, so the reaction can continue. It will vitrify for $y=y_2$ and the reaction will stop;

– if $T > T_{g\infty}$, crosslinking can be completed, since the material stays in its rubbery state from the beginning to the end.

However, in certain cases, particularly for materials having $T_g > 250°C$, it is possible for the degradation temperature T_D to be lower than $T_{g\infty}$. Thus, there is an optimal conversion ratio y_D which must not be exceeded so as to avoid degrading the material to the point of being unacceptable.

Experts use temperature, time, and transformation graphs (TTT), which add the time variable to the two variables of the graph in Figure 5.21. It must be simply recalled that the reaction is as slow as the temperature is low [PAS 02].

5.5. Mechanical properties

5.5.1. *Elastomers*

Elastomers are materials which are rubbery at room temperature. As we have already seen, for the T_g values to be low enough, the chains must be flexible and almost apolar, which is achieved in the case of polydienes, (natural rubber, polybutadiene) amorphous or slightly crystalline hydrocarbons polymers or copolymers such as:, polyisobutylene, ethylene-propylene copolymers, and more generally nonpolar or slightly polar polymers such as poly(dimethylsiloxane) e.g. silicone rubber, and certain halogen polymers: polychloroprene, fluorinated polymers and copolymers (Viton), etc.

To ensure that the materials do not creep, they are crosslinked (the term used in the profession is *vulcanized*). The vulvanized elastomer is, then, characterized by its crosslink density, expressed in terms of node concentration in the network or in the average molar mass of elastically active chains M_e .Let us recall that $x = \frac{2}{fM_e}$ where f, node functionality, is often equal to 4.

If the starting polymer is linear and characterized by a molar mass M_n, its shear modulus is given by:

$$G = G_0\left(1 - \frac{2M_e}{M_n}\right)$$

The term $\frac{2M_e}{M_n}$ can be considered as the effect of dangling chains. G_0 is the modulus of a network based on a linear polymer of infinite length, with the same node concentration.

Rubber elasticity, also known as entropic elasticity or hyperelasticity, displays the following characteristics.

1) *non-linear elasticity.* The behavior law, in the basic theory, takes the following form at equilibrium e.g. for a low strain rate:

$$\sigma = \frac{RT\rho}{M_e}(\Lambda^2 - \Lambda^{-1})$$

where Λ is the draw ratio defined by $\Lambda = \frac{l}{l_0}$.

Experts often use force f on the initial section s_0 of the test-piece:

$$\frac{f}{s_0} = \frac{RT\rho}{M_e}(\Lambda - \Lambda^{-2})$$

These relationships characterize an ideal network. In the case of a real network, we use the Mooney-Rivlin equation:

$$\frac{f}{s_0} = (C_1 + C_2\Lambda^{-1})(\Lambda - \Lambda^{-2})$$

where $C_1 = \frac{RT\rho}{M_e}$ and $C_2\Lambda^{-1}$ is the corrective term. Some theories predict that $C_1 \sim C_2$. However, C_2/C_1 tends to decrease when the crosslink density increases, or when the elastomer is swelled by a solvent.

2) *The modulus is proportional to the absolute temperature,* which shows that, in a thermodynamic balance of deformation, the entropic term widely dominates the internal energy term, hence the name of entropic elasticity and the interest taken by thermodynamicists in this original kind of behavior.

3) *Strains occur at constant volume,* Poisson's ratio is very close to 0.5.

4) *Strain is reversible, even on very large strains* (Figure 5.22).

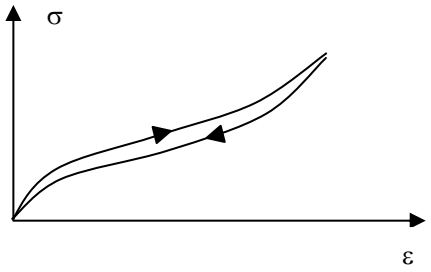


Figure 5.22. *Shape of the stress curve – strain during a loading/unloading cycle of an elastomer. The hysteresis is linked to the material's viscoelasticity*

The stress/strain curves often demonstrate the existence of a final hardening not taken into account by the equations shown above. Crystallization induced by chain stretching is one of the possible causes for this phenomenon (Figure 5.2).

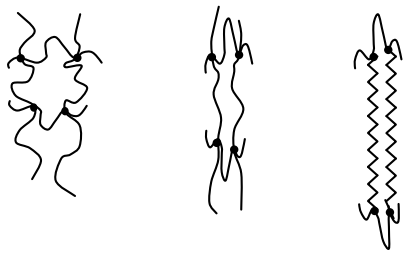


Figure 5.23 *Diagram of crystallization by stretching. This orientates the chains and creates an order which promotes crystallization*

Pure elastomers are sometimes relatively brittle, but adding fillers such as carbon or silica greatly increases their resilience. The theory predicts that the critical rate of elastic energy release in mode 1, G_{1c}, characterizing the resistance to crack propagation, should vary (as with the draw ratio at break Λ_R) proportionally to the square root of molar mass M_e of elastically active chains:

$$G_{1c} \alpha \Lambda_R \alpha M_e^{1/2}$$

In truth, although these equations accurately predict these trends, real elastomers can divert significantly from these relationships.

The mechanical behavior of elastomers at low strains obeys a *principle of tine/temperature equivalence*, which is expressed as follows:

$$\mathbf{P}(t,T) = \mathbf{P}(t/a_T, T_R)$$

where **P** is the considered property, T_R is an arbitrary reference temperature, and a_T is a shift factor which only depends on temperature.

Williams, Landel and Ferry showed in the 1950s [WIL 53] that a_T varied with the temperature according to the law known as WLF :

$$\text{Log } a_T = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)}$$

On the other hand, these authors showed that if T_R was taken to be equal to T_g , then C_1 and C_2, would take a quasi-universal values: $C_{1g} \sim 17.4$ and $C_{2g} \sim 51.6$ K. In fact, we find that in scientific literature, there are some C_{1g} and C_{2g} values which significantly move away from these values. However, their ratio does not seem to move away from $C_{2g}/C_{1g} \sim 3$K. Let us note the identity of C_{2g} with the values of C_2 which are specific to the free volume theory, or the theory of entropy (section 5.2.5). This result is not a coincidence. The WLF law can easily be established from free volume or entropy considerations.

Note that by calling $T_\infty = T_g - C_{2g}$, the WLF law then becomes:

$$\text{Log } a_T = A \exp \frac{B}{T - T_\infty}$$

with $A = \exp(-C_1)$ and $B = C_1C_2$. This equation is thus known as the Vogel law.

The WLF law can also be written:

$$\text{Ln } a_T = \frac{-2{,}3\ C_1\left(1 - \frac{T_g}{T}\right)}{1 - \frac{T_g - C_2}{T}}$$

meaning:

$$\frac{d(\text{Ln } a_T)}{d\left(\frac{1}{T}\right)} = \frac{2{,}3\ C_1C_2}{\left(1 - \frac{T_g - C_2}{T}\right)^2}$$

In a narrow temperature interval around T, we may consider that a_T obeys the Arrhenius law, with the apparent activation energy E_a, such as:

$$\frac{d(\text{Ln } a_T)}{d\left(\frac{1}{T}\right)} = \frac{E_a}{R} \qquad \text{either:} \qquad E_a = \frac{2{,}3\ RC_1C_2}{\left(1 - \frac{T_g - C_2}{T}\right)^2}$$

or, at $T = T_g : E_a(T_g) = 2{,}3\ R \frac{C_1}{C_2} T_g^2 \approx 6\ T_g^2$

Effectively, we observe that E_a (T_g) is of the order of several hundreds of kilojoules/mole and that it tends to increase with T_g.

5.5.2. *Mechanical properties of glassy amorphous polymers*

5.5.2.1. *Elastic properties*

Elastic behavior is characterized by four measurable quantities: compressibility modulus **K**, shear modulus **G**, Young's modulus **E** et Poisson's ratio **ν**.

The continuum mechanics allows us to establish relationships between these quantities:

$$E = 3K(1 - 2\nu) \qquad G = \frac{3(1 - 2\nu)}{2(1 + \nu)}K \qquad G = \frac{E}{2(1 + \nu)}$$

Knowing two of these quantities is sufficient for the two others to also be known. K and G can be considered as fundamental quantities which determine the values of E and ν. The variation of moduli with temperature is set out in a diagram in Figure 5.24a. Poisson's ratio is shown in Figure 5.24b.

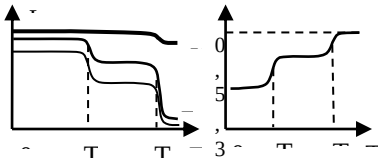


Figure 5.24. *diagram of modulus variation (a) and of Poisson's ratio (b)with temperature*

The modulus M at an unspecified temperature T in glassy state can be expressed as:

$$M = M_{00}(1 - \alpha T) - \sum_{0}^{T} \Delta M_i$$

where:

− M_{00} is the modulus at 0 K;

− α is in the order of $1/(2T_g)$, in other words the extrapolated glassy modulus at T_g is approximately half of modulus 0 K;

− ΔM_i is the modulus jump corresponding to the i^{th} secondary transition below the test temperature;

The compressibility modulus K is not influenced by secondary transitions. Essentially it depends on the cohesive energy density :

$K = K_{00}(1-\alpha T)$ with $K_{00} \sim 20\ d_e$

K decreases by a factor of approximately 2 across T_g.

The shear modulus G_{00} at 0 K also exclusively depends on cohesion. However, with the difference of K, it is affected by localized molecular movements, which are responsible for secondary transitions. These movements are characterized by the frequency f which increases with thermal agitation according to Arrhenius' law:

$$f_i = f_{i0} \exp\left(-\frac{E_i}{RT}\right)$$

where : f_{i0} and E_i characterize the i^{th} transition.

To study secondary transitions, we generally use dynamic mechanic analysis (DMA), or dynamic mechanical thermal analysis (DMTA) methods, which consist of the following principles: the transition is observed at temperature T_i such as the strain frequency f_{si} equal to the frequency of the considered molecular movement. It is either:

$$f_i = f_{si} = f_{i0} \exp\left(-\frac{E_i}{RT_i}\right)$$

or, for two different frequencies f_{si1} and f_{si2}:

$$\frac{1}{T_{i1}} - \frac{1}{T_{i2}} = \frac{R}{E_i} \mathrm{Ln}\left(\frac{f_{si1}}{f_{si2}}\right)$$

We see that the transition temperature T_i displacement linked to a given frequency variation is as big as the activation energy is small.

For example, let us consider the case of transition γ for a polyethersulfone (PES) type aromatic polymer: T_γ = 160 K for f = 1 Hz. If the same transition is measured by ultrasound at f = 10^7 Hz, the application of the above equation gives T_γ = 289 K because for this type of material E_γ = 48 kJ.mol^{-1}.

The main transition T_α associated with the glass transition is characterized by an apparent activation energy of several hundreds of kilojoules/mole. (Figure 5.25).

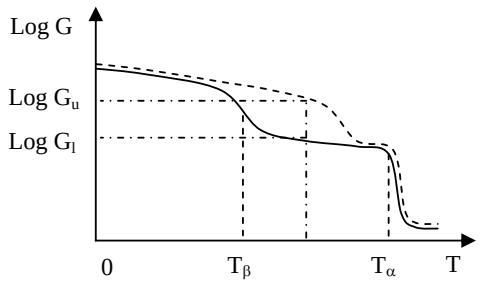


Figure 5.25. *Shape of the shear modulus variation with the temperature for two different frequencies*

– If, at low frequency (full curve), $T_\beta < T_{amb}$ (room temperature), then relaxation β is total at T_{amb}: the corresponding modulus G_l is the « relaxed » modulus.

– If the frequency is sufficiently raised (dotted curve), T_β will be higher than T_{amb}. The corresponding modulus will then be the « unrelaxed » modulus G_u.

Secondary transitions differ from one to other by their temperature at a given frequency, by their activation energy, and by the corresponding modulus jump $\Delta G = G_u - G_l$.

Some relaxations are very important mechanically (ΔG important). For example, this is the case for polymers with aromatic cycles in the chain, such as polycarbonate and polysulfones, whose most important secondary transition is found at -100°C at 1 Hz.

Other relaxations are not very mechanically active (ΔG weak). This is the case for polystyrene, for example, which also has a secondary transition towards -100°C, but with a low modulus jump.

Localized chain motions responsible for secondary relaxation can affect strongly the modulus at ambient temperature. For instance polycarbonate or aromatic polysulfone, which have a strong β transition, have a modulus E ~ 2.4-2.6 GPa. Polystyrene is stiffer (E ~ 3 GPa) despite its lower cohesive energy density, because it displays a very low local mobility.

These same relationships make Poisson's ratio vary more or less strongly around the secondary transitions, as indicated in Figure 5.24. Typical values are in the order of 0.35-0.37 in an unrelaxed state and 0.40-0.42 at room temperature for polycarbonate-polysulfone type polymers which display a relatively intense sub-glass relaxation.

All the above observations are valid for thermoplastics as well as for thermosetting materials.

5.5.2.2. *Yield and fracture properties*

The yield stress corresponding to the onset of plasticity σ_y (Figure 5.26) is essentially linked to the polymer's rigidity. At weak strain speeds, typically:

$$\sigma_y \approx \frac{E}{40}.$$

σ_y depends on the strain rate $\dot{e}$ and on the temperature according to Eyring's law :

$$\frac{\sigma_y}{T} = \frac{R}{V}\left(\mathrm{Ln}\,\dot{e} - \mathrm{Ln}\,\dot{e}_0 + \frac{E_y}{RT}\right)$$

where $\dot{e}_0$, E_y and V are characteristics of the material. V (activation volume) is generally of the order of 1 $L.mol^{-1}$.

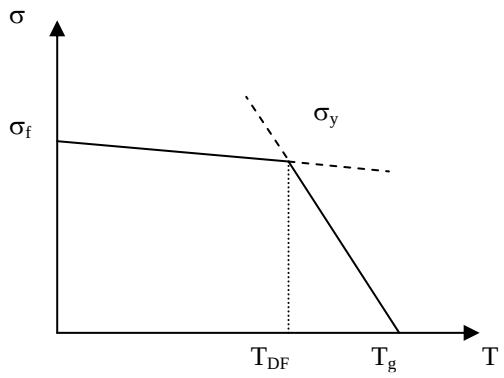


Figure 5.26. *Diagram of the competition between fragile and ductile processes*

It must be pointed out that σ_y also depends on the history of the material, and tends to increase according to the physical aging time (thermal aging between T_β and T_g).

Fracture behavior can be described as resulting from a competition between a brittle process (characterized by a stress σ_F which is hardly dependent on the temperature) and a ductile process (characterized by the yield stress σ_y decreasing in a quasi linear fashion with temperature (Figure 5.26).

This leads us to define a ductile-brittle transition temperature T_{DF} and an interval of ductility temperature: $\Delta T = T_g - T_{DF}$.

We can observe that certain polymers like polycarbonate or polysulfones have a very wide interval of ductility (> 200°C). Others such as polystyrene or PMMA have a very narrow (~ 10°C) and practically unusable ductility interval.

We notice that polymers with a wide ductility interval are characterized by an intense β transition, well separate from the glass transition. Additionally, these polymers are characterized by highly tortuous chains (C_∞ low). On the other hand, polymers with ductility interval are characterized by a weak β transition, close to the T_g. These polymers, whose prototype is polystyrene, have in common a higher chain characteristic ratio (C_∞).

Wu [WU 90] proposes the following empirical equation:

$$\frac{T_{DF}}{T_g} = (0.135 \pm 0.027) + (0.082 \pm 0.004) C_\infty$$

In organic glass, brittle rupture is generally preceded by crazing: the lips of microcracks are put back together by fibrillae where the polymer has been subjected to an important localized plastic strain. Crazing is disadvantaged by a weak C_∞, by crosslinking, by chain orientation.

With regard to fracture mechanics properties, we can distinguish fragile polymers (F) and ductile polymers (D).

For family F :

$$\text{Log } K_{1c} \sim 0.5 \text{ Log } \sigma_R - (0.9 \pm 0.4)$$

σ_R is the fracture stress under tension.

For family D:

$$\text{Log } K_{1c} \sim (1.0 \pm 0.3) \text{ Log } \sigma_y - 1$$

σ_y is the yield stress, K_{1c} is expressed in MPa.m$^{1/2}$ and σ in MPa.

For family F, K_{1c} generally varies between 0.6 and 1.2 MPa.m$^{1/2}$. For family D, K_{1c} varies between 0.8 et 10 MPa.m$^{1/2}$.

We should remember that $G_{1c} = \frac{K_{1c}^2}{E}$ in a state of plane strain and that $G_{1c} = \frac{(1-\nu^2)K_{1c}^2}{E}$ in a state of plane stress. For ductile polymers ($\nu > 0.4$), the two values differ slightly. G_{1c} values generally vary between 100 and 10^4 J.m^{-2} for most of industrial (unreinforced) polymers.

5.5.2.2.1. Behavior under fatigue

To our knowledge, there is no synthesis on the relationships between structure and properties under fatigue. However, we do know that, for glassy amorphous polymers, crazing is often responsible for a relatively weak endurance limit, often smaller than half the yield tensile stress. Crosslinking which disfavors crazing, generally allows for an improvement to fatigue resistance. Let us remember in addition that, in the case where materials have a T_g which is close to the test temperature, we can observe failure due to self-heating, particularly under high strain frequencies.

5.5.3. *Mechanical properties of semi-crystalline polymers*

5.5.3.1. *Elastic properties*

In section 5.2.5 we saw the shapes of temperature variation of a 100% crystalline elastic modulus, 100% amorphous or x_c% crystalline fictive polymer. In every solid state, the modulus is an increasing function of crystallinity ratio. However, this dependence is moderate in glassy state, whereas it is very strong in the rubbery state.

In the glassy state of amorphous phase, we often consider that the increase of the modulus is connected to the excess cohesion brought by the crystalline phase. The excess cohesion is similar to H_f melting enthalpy.

$$K = b\left(d_e + x_c \frac{H_{f0}}{V}\right)$$

where :

b is a parameter to the order of 10 at room temperature

d_e is the cohesive energy density

x_c is the crystallinity ratio

H_{f0} is the polymer's enthalpy of melting, expressed in $J.mol^{-1}$

V is the molar volume of a structural unit whose molar enthalpy of fusion is H_{f0}.

Generally:

$$0.1 d_e \leq \frac{H_{f0}}{V} \leq 0.9 d_e$$

In other words, crystallization increases the modulus by a factor smaller than 2, with regard to the amorphous glassy phase.

If the amorphous state in rubbery state ($T > T_g$), the crystalline phase is around 1,000 times more rigid than the rubber phase. As a first approximation, we can say that the modulus (shear or tensile mode) tends to be proportional to the crystallinity ratio. For example, the Young modulus at room temperature of polyolefins in rubber amorphous phase is in the order of:

0.15 to 0.30 GPa for PEbd

0.40 to 1.20 GPa for PEhd

1.1 to 1.6 GPa for PP

against 2 to 4 GPa for current glassy amorphous polymers, and a few MPa for the corresponding rubber phases.

Semi-crystalline polymers are different from glassy amorphous polymers essentially by their softening temperatures (HDT = *Heat Deflection Temperature*).

In the case of amorphous polymers, the HDT is close to the glass transition, typically:

$$HDT \sim T_g - \Delta T \qquad \text{with } \Delta T = 5 \text{ to } 10°C$$

We will note that HDT may vary in some degrees according to the measuring conditions, particularly the applied load.

In the case of semi-crystalline polymers, HDT is generally higher than T_g (Table 5.4).

Polymer	**T_g (°C)**	**HDT (°C)**	**T_f (°C)**
PE bd	-41	60	120
PE hd	-40	80	135
PP	0	100	165
POM	-50	125	177
PA 6 or 6.6	50 - 60	80 – 100	220 or 250
PET	80	85	255
PPS	88	260	288

Table 5.4. *Temperatures of glass transition, heat deflection, and melting of a few semi-crystalline polymers*

The example of PE shows that HDT is an increasing function with crystallinity ratio.

The example for PET demonstrates that when crystallinity ratio is relatively low, HDT values remain close to T_g.

5.5.3.2. *Yield and fracture properties*

As for glassy amorphous polymers, the stress at yield σ_y is almost proportional to the modulus and therefore to the crystallinity ratio for rubbery amorphous phase polymers. For example, in the case of polyethylene:

$$\sigma_y \sim 0.04\ E$$

We generally allow that the temperature and strain rate effects on σ_y can be represented by Eyring's law. However, at least for PE, many molecular flow mechanisms can coexist, each dominating in a certain strain rate and temperature domain.

When the plastic yield is approached, the chains present in the amorphous phase and interconnecting the crystalline lamellae ("tie chains") stretch and are able to reach their maximum extended length at the yield. Then, we can observe a variety of phenomena:

– if the interlamellar distance l_a is too small (meaning the sample has a high crystallinity ratio), then plastic strain is impossible, the fracture is brittle. For example, in PE, the fracture is systematically brittle as soon as $l_a \leq 6$nm. This is why in applications such as gas or water piping, copolymers ethylene-butene, ethylene-hexene or ethylene-octene are used. The higher olefin, used in low concentrations, creates disorder in the chain and limits crystallinity to improve resilience;

– If the crystals are not very cohesive, then the tie chains can extract the segments which make them from the lamellae. The material becomes amorphized, plastic strains which can stretch the chains may occur, the material is ductile;

– In some cases, however, a cavitation process can occur in the amorphous phase, and acts as the initial stage of a brittle or semi-brittle fracture. We observe crazing in semi-crystalline polymers. This generally differs from the crazing found in amorphous polymers because the fibrillae are bigger;

– Finally, in some cases of slow strain, for example under fatigue, the fracture propagates in the interspherolitic zone. Examinations under the microscope reveal a "washing away" of the spherulites. Here also, we are dealing with brittle behavior. Practitioners know that spherulites with strong dimensions must be avoided.

Analyzing molecular mechanisms of semi-crystalline polymer fractures is relatively complex. With the thickness of the interlamellar amorphous layer and the "tie chains" density aside, the entanglement density in the amorphous phase, the chain length and the surface energy of the amorphous phase seem to play an important role.

Generally, semi-crystalline polymers have a better resistance to fatigue than amorphous polymers, which allows us to imagine using some of them for making hinges (for example, built-in caps on shampoo bottles made of polypropylene). With regard to high-performance composites, the semi-crystalline PEEK matrices offer the highest resistance to fatigue (aeronautic applications).

5.6. Plasticizers and impact modifiers

There are two types of additives which are frequently used in order to change the mechanical behavior of polymers: plasticizers and impact modifiers. In both of these, the mass fraction of the additive can reach several tens of percentages.

5.6.1. *Plasticizers*

Plasticizers are additives miscible in the polymer, therefore they are at least partially solvents. Their main characteristic, other than miscibility, is having a glass transition temperature T_{gs} which is lower than polymer one T_{gp}. When mixed into the polymer, these additives decrease the glass transition temperature. Let T_g be the glass transition temperature of the mixture, v_s and $(1\text{-}v_s)$ the respective volumefraction of the plasticizer and the polymer, and let α_s and α_{pb} be the respective coefficients of the free volume expansion:

$\alpha_s = \alpha_{ls} - \alpha_{gs}$ and $\alpha_p = \alpha_{lp} - \alpha_{gp}$

where α_l and α_g represent the expansion coefficients in the liquid/rubbery state and glassy state, respectively.

The theory of free volume leads to:

$$T_g = \frac{(1 - v_s)\alpha_p T_{gp} + v_s \alpha_s T_{gs}}{(1 - v_s)\alpha_p + v_s \alpha_s}$$

Simha and Boyer showed that for polymers:

$\alpha\, T_g \sim 0.113 = \text{constant}$

By inserting this equation into the preceding formula, we obtain:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + A\, v_s \quad \text{where :} \quad A = \frac{1}{T_{gs}} - \frac{1}{T_{gp}}$$

A is a parameter which characterizes the plasticizer efficiency . Typical values of A for PVC plasticizer: $(1.5 \text{ to } 3).10^{-3}\ K^{-1}$.

In a given structural family, T_g is low when the molar mass is low. We understand why butyl phthalate is a more efficient plasticizer than didecyl phthalate, which is a more efficient plasticizer than an aliphatic polyester with a molar mass of 1 to 2 $kg.mol^{-1}$. However, butyl phthalate is very volatile and migrates easily, whereas the polymer plasticizer does not migrate. We can see that all industrial plasticizers are made of a compromise between the need for a certain level of efficiency (represented by factor A) and a reasonable resistance to migration. In current applications of plasticized PVC (flexible water hoses), the dioctyl phthalate may be sufficient. In more demanding applications in terms of durability (insulation for cables in nuclear plants), superior phthalates are preferable (didecyl, ditridecyl, etc). In some critical applications (use in contact with hot water) we can be led to use polymer plasticizers, but by resigning ourselves to a weak plasticizing efficiency.

The modulus-temperature curves of a plasticized polymer and of the same unplasticized polymer take the following shape seen in Figure 5.27.

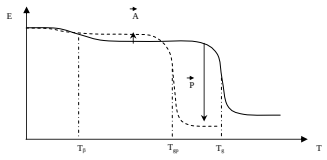


Figure 5.27. *Shape of the modulus variation with temperature in the case of an unplasticized polymer (continuous line) and plasticized (dotted line).* $T_\alpha \sim T_g$

The previous considerations show that plasticization can be explained by a decrease in T_g.

A more unexpected yet general effect is anti-plasticization: an increase in the modulus at the glassy plateau linked to the fact that plasticization partially prevents the β transition. This behavior has been observed as well in PVC as in polycarbonates, polysulfones or epoxy networks.

Plasticization can be external as well as internal. For example, incorporating by copolymerization vinyl acetate (T_g of PVAC: 40°C) into PVC (T_g = 80°) will plasticize the PVC (floor coverings, etc.). Internal plasticization is currently used frequently in the thermoset industry. In semi-crystalline polymers, plasticization is rarer. However, it is frequently used in polyamides 11 or 12 (aromatic

sulfonamides). We, also, use plasticizers (oils) in elastomers, but in most cases, the real objective is not plasticization.

5.6.2. *Impact modifiers*

Impact modifiers are generally polymers which are non-miscible in the receiving polymer. They can be incorporated as external additives, mixed and dispersed mechanically. Or, they can be added as internal additives (non-miscible sequences in a copolymer block). Their fortuitous discovery was made over more than 50 years ago, when scientists were starting to realize that by mixing an elastomer (flexible, ductile) into a plastic (rigid, brittle), such as polybutadiene into polystyrene, a material with decreased rigidity but in acceptable proportions was obtained, whereas the strength and impact resistance were increased in considerable proportions (Figure 5.28).

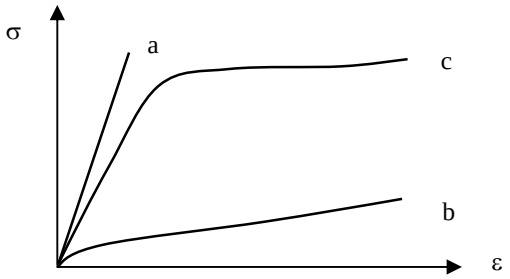


Figure 5.28. *Diagram showing stress-strain curves of the receiving polymer (a) of the elastomeric modifier (b) and of the blend (c)*

Such properties however are only obtained when the blend morphology fulfills certain conditions: generally, we are looking for nodular morphologies (see section 5.2.5) with a certain combinations (modifier volume fraction) = f (nodule size).

For some time, research in this area was confined to polystyrene : PS-PB blends, block copolymers , ABS type terpolymers, etc. It was then noticed in the 1970s that this approach could be generalized for all polymers: ABS as an impact modifier for PVC building profiles, EPR for polypropylene for car bumpers, polysuflones for structural adhesives, EPR for polyamides, etc.

Strengthening mechanisms have been the subject of a lot of research which has allows us to highlight the following mechanisms:

– Stopping crack propagation by nodules (crack blunting) ;

– Nodules favor local shearing and nucleate diffuse shear bands which absorb a lot of energy.

That these two phenomena coexist may explain the interest in bimodal distributions of nodal sizes. The small nodules initiate shear bands, and the large nodules stop the cracks.

For an impact modifier to be efficient, it has to stick to the matrix so it prevents any decohesion. Adhesion is optimal in block copolymers because covalent bonds unite the blocks.

For polymer blends which are unbound from the beginning, chemical functions can be inserted into the additive, which promote "anchoring" onto the receiving polymer. This can be seen in the case of maleic anhydride grafted onto EPR, which ensures its bond with all kinds of polar polymers.

In some cases, a third body will preferably be put on the interface and ensure the bond between two phases. As an example, let us consider two non-miscible polymers called A and B. The third body could be a block copolymer $–(A)_n– (B)_p –$ .Sequence $–(A)_n–$, which is miscible with polymer A will become entangled in the chains of A. Sequence $–(B)_p–$ will do the same with B: the block copolymer will act as a fastener, binding the two phases together.

We are able to judge the efficiency of an impact modifier in a polymer by the variation in resilience (Figure 5.29) or the toughness that it induces at room temperature. The displacement of the ductile-brittle transition temperature (towards low temperatures) is also a good criterion (Figure 5.30).

In the last thirty years, the market for impact modifier has rapidly developed. The only thing which stands in the way of their expansion could be an eventual hardening of the limits connected to recycling, which is of course not an easy option for polymer blends.

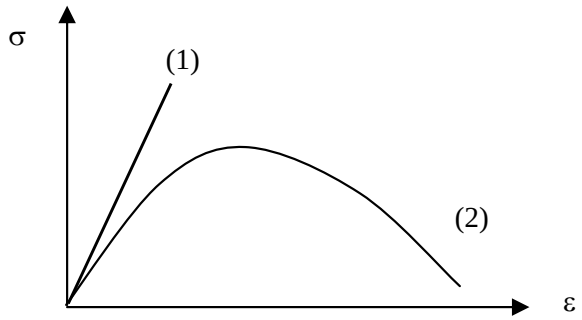


Figure 5.29. *Stress-strain curves (instrumented impact) by a brittle polymer (1) and the same polymer by impact modifier (2)*

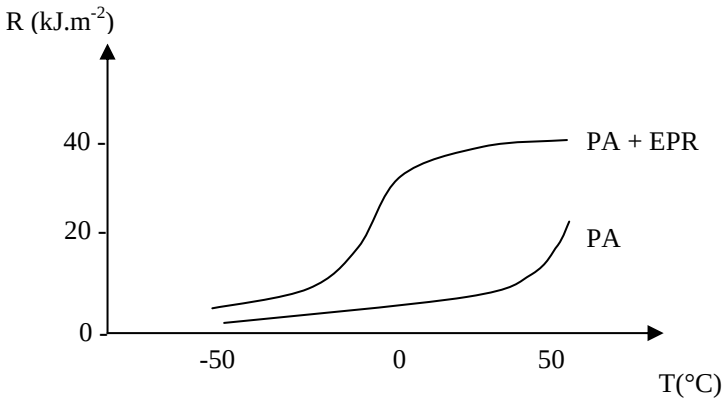


Figure 5.30. *Resilience according to temperature for a polyamide (PA) and the same polyamide reinforced by EPR*

5.7. Properties of a few industrial linear polymers

Polymer	**Acro-nym**	**Type** (a)	T_g **(°C)**	T_f **(°C)**	d_a (b)	d_c (c)	**E (GPa)**(d)
Low density polyethylene	PEbd	C	-43	120	0.85	1.00	0.2-0.3
High denisty polyethylene	PEhd	C	-43	140	0.85	1.00	0.8-1.2
Polypropylene	PP	C	-3	192	0.85	0.95	1.1-1.6
Polyoxymethylene	P0M	C	-50	177	1.25	1.54	2.9-3.4

Polyamide 6	PA6	C	50	223	1.08	1.23	3.2
Polyamide 6,6	PA66	C	50	250	-	-	2.6
Polyamide 11	PA11	C	27	190	1.01	1.18	1.0
Ethylene polyterephthalate	PET	C	80	255	1.33	1.46	2-9
Polybutylene terephthalate	PBT	C	60	227	-	-	2.5-2.8
Polyphenylene sulfide	PPS	C	85	288	1.34	1.46	-
Polyether ether ketone	PEEK	C	141	337	1.26	1.32	3.6
Polyvinyl chloride	PVC	A	80		1.39	-	3.0
Polystyrene	PS	A	105		1.05	-	3.3
Polymethyl methacrylate	PMMA	A	127		1.18	-	3.3
Polycarbonate	PC	A	150		1.20	-	2.4
Polysulfone	PSU	A	190		124	-	2.6
Polyethersulfone	PES	A	210		1.37	-	2.7
Polyetherimide	PEI	A	210		1.27	-	3.1
Polyoxyethylene	PPO	A	210		1.07	-	2.4
Polyphthalamide	PPA	A	127		1.15	-	2.4
Polyamideimide	PAI	A	275		1.42	-	4.9

Table 5.5. *Properties of a few industrial linear polymers*

NOTES –

− (a) semi-crystalline type (C) or amorphous (A);

− (b) amorphous-state density;

− (c) crystalline-state density;

− (d) sample modulus used under industrial conditions;

− (e) dry-state material modulus. Great decrease in humid state

− (f) modulus greatly varying with orientation: 2 GPa for isotropic part, 9 GPa for strongly oriented fiber.

5.8. Conclusion

The cost of industrial polymers spreads between about 1 and 100€/kg. Indeed, commercialized tonnage is a function which greatly brings down the cost. Experts generally distinguish three classes of polymers: special polymers (such as thermostable polymers used in aeronautics or polymers for medical use); engineering polymers whose cost may vary between a few and several tens of €/kg (e.g. polyamides, polycarbonate, etc.) and commodity polymers (polyethylene, polyvinyl chloride, polystyrene, etc.) whose cost does not exceed a few €/kg. Evidently, building and civil engineering sectors are only interested in two of these

categories; technical polymers for relatively low volumes of applications: waterproofing, concrete additives, etc., and commodity polymers for a high volume of applications: thermal insulation, window profiles, pipes, packaging, etc.

Compared to metals, synthetic polymers are young materials, only appearing around 50 years ago. But we can already see that their evolution has followed a different path. The history of metallurgy was first of all to research the best performances:

Native copper → bronze → iron → steel → special steels, etc.

The history of plastics processing was rather to research the best compromise between cost and performance. Of course, we can cite the spectacular successes of polymers as an example in their competition with traditional materials: polyamides replacing silk parachutes, polypropylene to replace the steel of car bumpers, epoxy-carbon composites to replace aluminum used in helicopter blades, etc... However, a large proportion of the current research effort is dedicated to the competition between plastics themselves. The fundamental question is: can we replace a polymer costing 20€/kg with a polymer which costs 2€/kg? An overview of scientific and technological literature shows us that the most "advanced" materials in this domain, meaning the object of the most intense research, are not characterized by the highest intrinsic performances. These are rather common polymers with mediocre performances, but, however, offering a compromise: ease of processing against usage properties and unbeatable costs.

We can easily see that this trend will increase in the futures and win over all the material families because economic constraints will weight down more and more on the following chain: synthesis → processing → use. Can a miracle, such as the (fortuitous) invention of polyethylene happen again? Theoretically, it is possible but seems improbable after more than 70 years of systematic research in macromolecular synthesis. The domain will not remain stagnate for as much: progress in knowledge will allow for a more and more tight structure control (on all scales) during synthesis and implementation. Researchers will continue to exploit the quasi infinite combinatory offered by the diversity of polymers (and for a given polymer microstructure), additives, fillers, possibilities for reactive processing, etc...

The effects of this research allow us to accommodate for existing chemical families, perhaps for a long time to come, by trying to adapt them to the demands of sustainable developments (improvement in long term resistance, recycling). We will see new families of polymers emerge from "green" chemistry: vegetal or biochemically synthetic polymers. However, it is difficult to imagine these new materials being capable, one day, of supplanting the current common polymers.

Polymers are generally perceived as being bad by environmental activists, above all because of the massive and anarchic spreading of use packaging in natural areas. However, whatever the threats to the environment which weigh down on industrial civilization, from now it is impossible to imagine its future without polymeric materials.

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